

Emulsifier-Free Emulsion Copolymerization of Styrene with Methacrylic Acid

Ping-Hua Wang,^{1,2} Qian-Wen Wang¹

¹Department of Polymer Science and Engineering, Hefei University of Technology, Hefei, Anhui 230009, People's Republic of China

²Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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ABSTRACT: The study on batch emulsifier-free emulsion copolymerization of styrene with methacrylic acid was conducted. The copolymerization process was followed by gravimetry, infrared, and transmission electron microscopy. The copolymerization mechanism differs from that of styrene with acrylic acid. The effect of solid content on particle

size was examined, and it was found that the particle size was increased as the solid content was increased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1747–1751, 2003

Key words: emulsion copolymerization; copolymer microspheres; solid content

INTRODUCTION

Emulsifier-free emulsion copolymerization of oil-soluble monomers [mainly styrene (St)] with water-soluble comonomers has been widely used to produce monodisperse polymer microspheres with various surface functional groups. Therefore, many studies have been reported in order to understand the process of the copolymerization, and to monitor the type and distribution of functional groups.^{1–3} These functional polymer microspheres have found extensive applications in a number of fields.^{4–6}

Of the functional polymer microspheres, carboxylated copolymer microspheres, which are generally prepared by emulsion copolymerization of styrene with carboxylic acid monomers, belongs to an interestingly important class of industrial emulsion polymer system.^{7–9} Carboxylic acid monomers are often completely soluble in water. However, they will still distribute to varying extents into the organic phase, depending on their relative hydrophobicity. The most frequently studied acid monomers copolymerized with St are itaconic acid (IA), acrylic acid (AA), and methacrylic acid (MAA), listed in order of hydrophobicity.

Ceska copolymerized IA, AA, and MAA with St by emulsifier-free emulsion polymerization in separate reactions. Copolymerization rates were found to in-

crease with the presence of carboxylic acid monomers in the order of IA < AA < MAA.¹⁰ The rate increased as the hydrophobicity of the monomer increased.

Potentiometric and conductometric titration studies of the copolymer latex system of carboxylic acid monomers copolymerized with St has been conducted and reported in the literature.^{11–13} Most of the studies were aimed at determining the distribution of the acid monomers among the aqueous phase, particle surface, and particle interior, and to estimate the effect of the distribution on the rate of copolymerization, particle generation, and particle stability. Kinetic studies by means of gravimetric method together with or without gas chromatography were also reported with the end of reaching a kinetic model.^{8,15} However, a full and universal mechanism accounting for the copolymerization of styrene with water-soluble or functional comonomer(s) remains unresolved, most probably owing to the complexity of the copolymerization process and varying degree of hydrophilicity of functional comonomer(s).

Our group has initiated a systematic study on the copolymerization of styrene with a number of functional comonomers including some carboxylic acid monomers and acrylamide monomers.^{16–20} Additional attention was paid to use these functional polymer microspheres as supports for the formation and deposition of some metal particles such as palladium, nickel, and cobalt to prepare composite particles.^{16–18} In the latest report, the copolymerization behavior of St with AA was studied, and was found that in the initial period of particle growth stage, the polymerization of St was dominant, yielding particles with low content of AA unit. While after most of St was con-

Correspondence to: P.-H. Wang (phwang@mail.hf.ah.cn).

TABLE I
Components and Conditions for Copolymerization of St with MAA^a

Sample	St (g)	MAA (g)	KPS (g)	H ₂ O (ml)	Solid con. ^c (%)	Conver. ^d (%)	Diameter (nm)
MAA1 ^b	40	4	0.16	400	10	90.4	389
MAA2	40	4	0.16	267	15	92.9	
MAA3	20	2	0.08	100	20	91.0	417
MAA4	20	2	0.08	80	25	93.0	511

^a Polymerization temp.: 70°C; polymerization time 8h.

^b Samples were withdrawn in the polymerization process.

^c Solid content was calculated based on ratio of St vs amount of water.

^d Final total conversion.

sumed, the polymerization of AA became relatively significant.²¹ A shift of polymerization locus from "inside" the particle to "outside" the particle was proposed. However, in the copolymerization of St with MAA, a different behavior of copolymerization was observed. The results are reported here.

Experimental

Materials

St and MAA were purified by distillation under reduced pressure. Potassium persulfate (KPS) was of analytical grade and used without further purification. Distilled water was used in the experiments.

Copolymerization of st with MAA

Copolymerization of St with MAA was conducted by batch emulsifier-free emulsion copolymerization of St with MAA using KPS as initiator. The procedure of copolymerization is referred to in earlier reports.¹⁶⁻¹⁸ The recipes of the copolymerization are listed in Table I. The reaction was carried out under nitrogen atmosphere at 70°C with mechanical stirring. The latex was purified by repeating centrifugation.

Characterization

The total conversion of monomers was calculated by gravimetric method. MAA1 was chosen for study of the copolymerization process. For samples in the copolymerization course in MAA1, a small amount of emulsion was withdrawn at different intervals, and mixed immediately with a minor amount of hydroquinone. After weighing, the emulsion was then dried to determine the solid content, by which the total conversion was obtained. Meanwhile, a part of the above withdrawn emulsion was purified by dialysis for one week, and then dried for infrared (IR) analysis.

IR spectra were recorded on a Vector-22 IR spectrometer by KBr pellet. The size and morphology of copolymer microspheres were observed by transmis-

sion electron microscopy (TEM) on a Hitachi-800 microscope.

RESULTS AND DISCUSSION

Copolymerization process of st with MAA

Figure 1 shows the variation of total conversion of monomers during the copolymerization process in MAA1. With the polymerization proceeding, the conversion, as generally observed, increases rapidly in the initial period of polymerization (from beginning to about 4 h). And then, the conversion increases slowly, and gradually levels off at certain value.

The morphology of copolymer microspheres during the copolymerization process in MAA1 was observed by TEM and some photographs are shown in Figure 2. The corresponding particle size is given in Figure 3. The polymer microspheres are spherical, stable, and uniform in size along the copolymerization process. As observed in Figure 3, the particle size increases dramatically in the initial period from beginning of the polymerization to polymerization time at about 4 h. After this time, the increase in particle size becomes relatively gradual. The variation in particle size corresponds to that in conversion as shown in Figure 1. That is, in the initial stage of the copolymerization

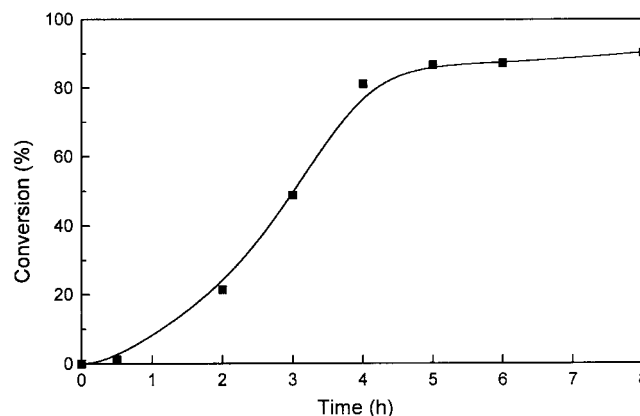


Figure 1 Rate of copolymerization vs polymerization time.

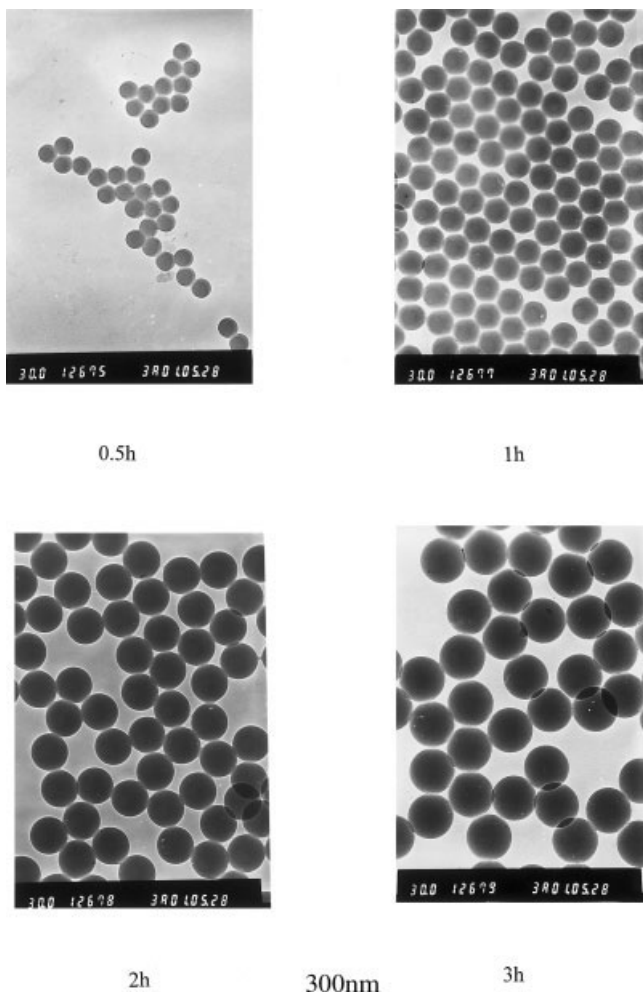


Figure 2 TEM photographs of copolymer microspheres during the polymerization process (MAA1).

(0–4 h), the copolymerization rate was fast, and therefore the particle size was significantly increased correspondingly; while during the later stage, the copolymerization rate slows down, leading to slow in-

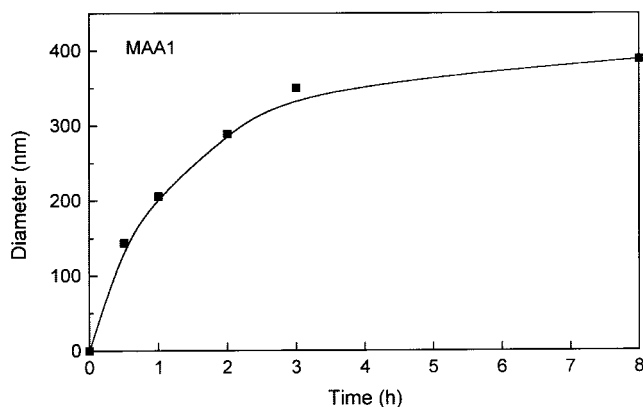


Figure 3 Variation of the diameter of copolymer microspheres vs polymerization time (MAA1).

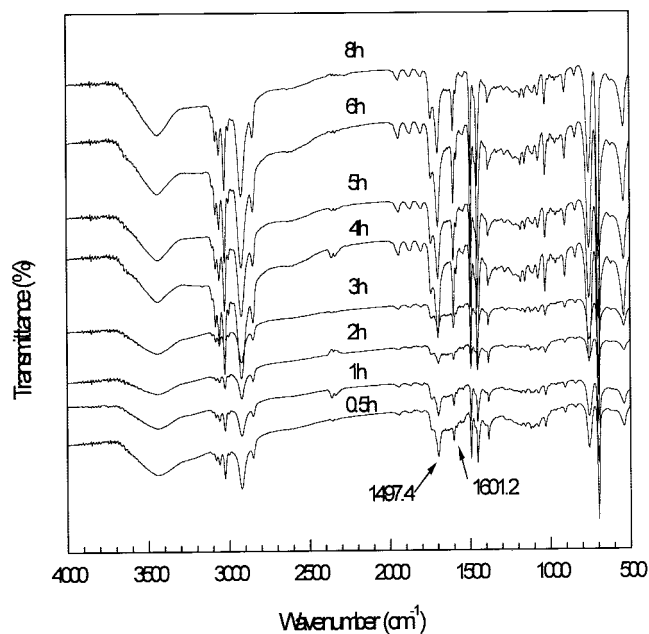


Figure 4 IR spectra of the copolymer microspheres during the polymerization process (MAA1).

crease in the conversion of monomers. As a result, the increase in particle size was slow.

The composition of copolymer microspheres during the copolymerization course in MAA1 was studied by IR. The spectra are shown in Figure 4. The spectra reveal well defined bands of styrene unit. A characteristic peak at about 1697 cm^{-1} is attributed to carbonyl stretching in the carboxyl group, indicating copolymerization of St with MAA. Because the peaks at 1697 and 1601 cm^{-1} are due to stretching of carbonyl bond and benzene ring, respectively, the comparison of intensities of these two peaks can qualitatively indicate the relative quantity of MAA and St in the microspheres. Examination of Figure 4 reveals that the relative intensity ratio of the two peaks does not show evidently significant variation during the copolymerization process. Even in polymerization at 0.5 h, the peak at 1697 cm^{-1} is quite strong in intensity, suggesting a measurable amount of MAA in the microspheres. The phenomenon observed here differs from that observed in copolymerization of St with AA as reported earlier.²¹ In the St/AA system, the AA content in the copolymer microspheres as revealed by IR spectra was relatively quite low in the initial period of the copolymerization.²¹ When the total conversion of monomers reaches high around about 80%, the AA content in the microspheres was significantly increased. A mechanism based on those results was proposed to describe the copolymerization process of St with AA. In the initial stage of polymerization, the polymerization of St was dominant and occurred mainly “inside” the particles, yielding particles rich in St. While in the later stage after most of St was con-

sumed, the polymerization of AA became relative important, which mainly occurred "outside" the particles due to its more hydrophilic nature, yielding a AA-rich shell. Shift of polymerization locus from inside the particles to outside the particles was proposed for the copolymerization of St with AA. The core-shell structure of St/AA microspheres was confirmed by X-ray photoelectron spectroscopy and elemental analysis.²¹

However, in the copolymerization of St with MAA as in this work, no significant variation of MAA content in the microspheres as revealed by IR spectra can be observed. This suggests a different polymerization mechanism for the St/MAA system from that for the St/AA system. A tentative scheme for the particle growth stage in the copolymerization of St with MAA is proposed here. After nucleation ended, which was supposed via a homogeneous nucleation mechanism,²² the polymerization locus was inside the particles, which was swollen by St. Because of relatively higher hydrophobicity of MAA, MAA could enter the particle to participate in the reaction by two ways: (1) directly diffusing into the particle in the form of monomer; (2) diffusing into the particle or captured by existing particles in the form of oligomers, which was formed in the aqueous phase by copolymerization with St. Both ways were possible. And as a result, MAA was copolymerized during the whole process without evident order in polymerization sequence. This suggests that polymerization was occurring in the particles, and no evident shift of polymerization locus occurred during the copolymerization process. However, due to hydrophilic nature of MAA, it tended to locate on the surface of particles when copolymerizing with St. As a result, the surface of the copolymer microspheres thus obtained is somewhat rich in MAA unit, as we reported earlier.²⁰ But because MAA was less hydrophilic than AA, the surface content of MAA units in St/MAA microspheres was markedly lower than the content of AA units in St/AA copolymer microspheres.²⁰ This, once more, suggests that some parts of MAA were copolymerizing inside the particles, and therefore were buried inside the particles. This inference supports the argument that polymerization was occurring in the particles during the copolymerization process.

Effect of solid content

As is expected, solid content in the emulsifier-free emulsion polymerization is limited compared to the counterpart in emulsion polymerization with emulsifier or surfactant because higher solid content in emulsifier-free emulsion may lead to agglomeration. This somewhat limits the application of emulsifier-free emulsion polymerization. In this work, copolymeriza-

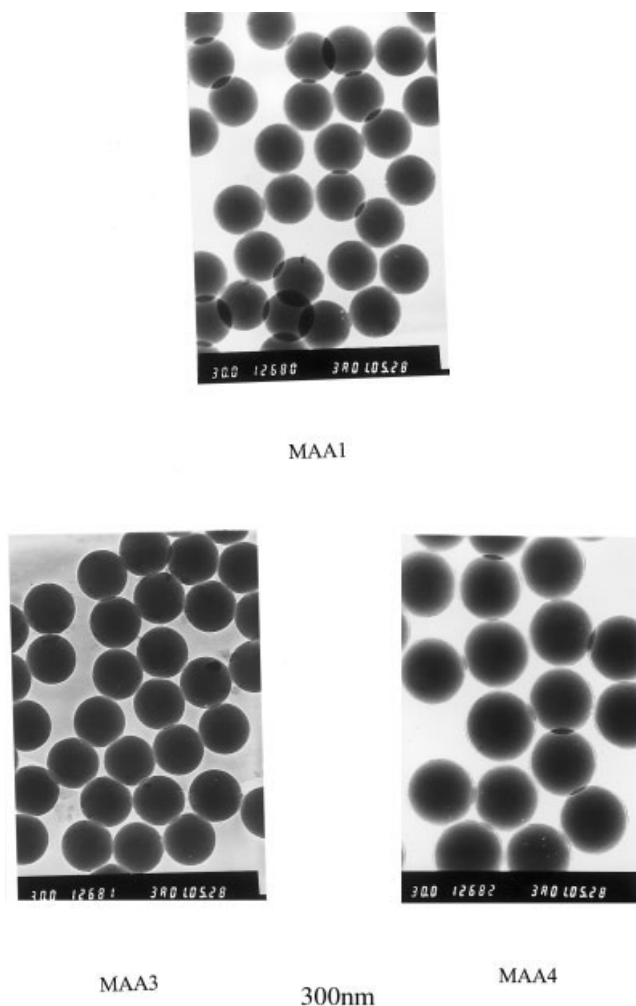


Figure 5 TEM photographs of copolymer microspheres.

tions of St with MAA of various solid contents were tried and their effects on particle size were examined.

The final total conversions of monomers at four solid contents are given in Table I. The general trend is that with an increase in solid content, the conversion increases, though not significantly.

The morphology of the copolymer microspheres under different solid contents was observed with TEM and shown in Figure 5. The particle size is listed in Table I. As seen in Figure 5, the microspheres are monodisperse in size in all cases. The particle size, on the other hand, shows an evident increase upon the increase in solid content. Increase in solid content means increase in concentration of both monomer and initiator. As a result, the rate of formation in oligomers would be increased, which should result in more primary particles according to the homogeneous nucleation mechanism. And this should lead to a decrease in particle size since the total amount of monomer is constant. However, when primary particles are formed, higher solid content means higher density of particles in the system. This would decrease the sta-

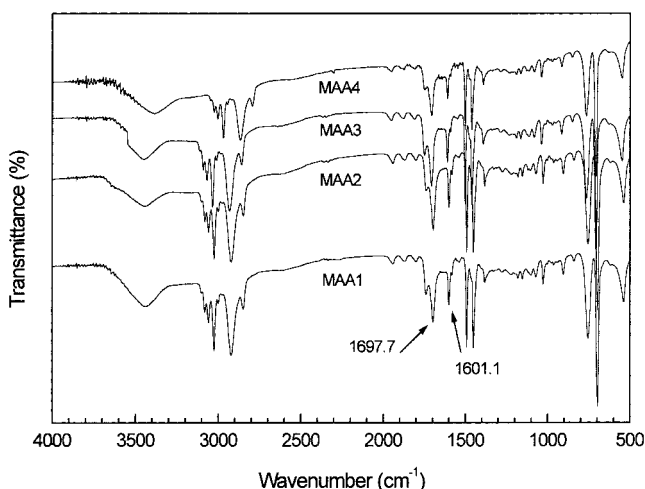


Figure 6 IR spectra of the copolymer microspheres.

bility of primary particles, and therefore chances of mutual collision and agglomeration of primary particles would be enhanced to form more stable particles. The result is that the number of particles is decreased and thereafter the final particle size is increased. From the results observed in this work, it appears that the latter effect overtakes the former effect so that the particle size decreases with an increase in solid content.

The composition of the copolymer microspheres was studied by IR. The spectra are shown in Figure 6. Except the typical peaks of St units, a relatively strong peak at about 1697 cm^{-1} appears in all spectra. This peak attributes to presence of MAA units. Comparison among these spectra suggests no significant difference. This is not difficult to understand because the spectra reflect only the final composition of the copolymer microspheres. Since the MAA/St ratio is the same in all polymerizations, and in addition, as discussed above, variation in solid content does not result in an evident difference in the final conversion, the

composition of the final copolymer microspheres is therefore similar in four cases.

CONCLUSIONS

The study on batch emulsifier-free emulsion copolymerization of St with MAA was conducted. The copolymerization process was studied by gravimetry, IR, and TEM. The results showed that the polymerization mechanism of St with MAA differs from that of styrene with acrylic acid as reported earlier. The effect of solid content on particle size was examined, and it was found that the particle size was significantly increased as the solid content was increased.

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